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WEST VIRGINIA UNIV MORGANTOWN DEPT OF CHEMICAL ENGIN--ETC F/G B/B  
MEASUREMENT OF AVAILABILITY RATE FOR TOTAL PHOSPHORUS FROM RIVE--ETC(U)  
JAN 78 F H VERHOFF, M HEFFNER, W A SACK DACW49-78-C-0011

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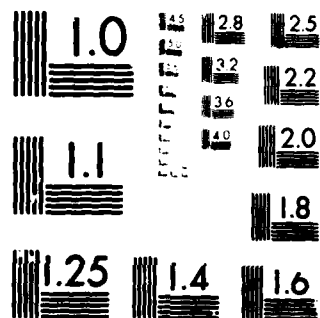


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The investigation of this availability question was divided into two parts; the chemical and the biological measurements. This section of the research is concerned with the biological studies, although the biological study samples were also analyzed chemically in the other part of the investigation. The biological tests as proposed in the contract were based upon previous knowledge of the weather activities in the Sandusky River basin and upon biological availability studies for lake sediments. In reality, the weather did not cooperate and the suspended materials in storm river water differed significantly from the suspended material found in lake sediments.

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**MEASUREMENT OF AVAILABILITY RATE FOR  
TOTAL PHOSPHORUS FROM RIVER WATERS**

by

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**January 1978**

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## ABSTRACT

The original goal of the research was to determine the maximum amount of total phosphorus from river storm events which could be converted into microbial biomass under lighted culture conditions. In addition, it was hoped that the rate of total phosphorus conversion could be obtained from the data. The net result of the experiments was that the rate was too slow to permit measuring the maximum conversion possible and only the rate of conversion was obtained.

The experimental procedure involved incubation and separation. At times equal to zero samples of water from various rivers were placed in lighted vats. The initial concentrations of total phosphorus, ortho phosphates, suspended solids, and other parameters were measured. The incubation was then permitted to occur with the indigenous microbial population. The microbial growth was observed and after a significant microbial population had accumulated, it was harvested. The microbes were centrifuged from the water which was decanted from the incubation vessels. Most of the inorganic suspended solids remained in the vessel. Further, any microbial growth which accumulated on the sides of the vessel was removed by scraping. The total phosphorus and the inorganic suspended solids in the solids removed from the vessel were then determined. The water was returned to the vessel and the incubation was continued. The dissolved oxygen concentration and the pH in the vessel were monitored during the entire incubation period.



The basic concept involved in the experiments is the conservation of mass on the two major quantities of interest, the total phosphorus and the inorganic suspended solids (fixed solids). The initial quantities of these two materials were determined and the amount removed during each harvest was measured. From these numbers it was possible to calculate the amount of total phosphorus which was converted to microbial biomass. From the time between harvests, the rate of conversion could be calculated.

The differences between this availability study and most previous ones can be attributed to harvesting procedure and the mass balance calculations. The harvesting procedure gave semi-direct measurements of the total phosphorus incorporated into the microbial population. Secondly, the harvesting procedure permitted a time succession of microbial species, each species growing and extracting phosphorus when the conditions were best for it. The mass balances could then be applied to this data to obtain the amount and rate of conversion from total phosphorus to available phosphorus.

Although the experiments utilized indigenous microbes, it was not intended to mimic the exact conditions in a lake or bay. However, the conditions used in the experiments should reasonably approximate some conditions under which this total phosphorus would be converted to biomass in natural waters. Probably the laboratory conditions would give a high estimate of the rate.

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## INTRODUCTION

The general goal of the contract was to measure the availability for biological growth of the total phosphorus transported during storm events into Lake Erie. This information was required because previous investigations by the Corps of Engineers (1975) indicated that most of the total phosphorus transport into Lake Erie occurred during the high flow events which happened most frequently in the spring of the year. The general productivity of Lake Erie could then be expected to depend upon availability of this transported total phosphorus.

The investigation of this availability question was divided into two parts; the chemical and the biological measurements. This section of the research is concerned with the biological studies, although the biological study samples were also analyzed chemically in the other part of the investigation. The biological tests as proposed in the contract were based upon previous knowledge of the weather activities in the Sandusky River basin and upon biological availability studies for lake sediments. In reality, the weather did not cooperate and the suspended materials in storm river water differed significantly from the suspended material found in lake sediments.

For the biological studies, samples were to be drawn from several rivers during storm events which would occur in November 1976, February 1977, and April 1977. The weather failed to cooperate and the first storm event from which samples were obtained was in March of 1977. Thus, the studies were set back significantly in timing.

From previous work on lake sediments it was expected that the time span for release of nutrients from the suspended materials would be about one to two months and that specific strains of algae could be selected for the biological uptake. The strains of algae typically used in the Algal Assay Procedure were obtained from the EPA Laboratory in Corvallis, Oregon, and were grown in a culture to a phosphorus starved state. However, when these algae were added to the storm water from the rivers, no growth occurred and in fact the algae appeared to die. Upon letting the river water stand for some period of time under lighted conditions, an indigenous population of phytoplankton began to grow. Since the availability studies really were not dependent upon the species of algae, the indigenous phytoplankton was satisfactory. Secondly, the time span for the release of most of the biologically available phosphorus was much longer than anticipated - thus the time of the grant was insufficient to obtain that fraction of the total phosphorus which would eventually be available for microbial growth. However, since the rate of total phosphorus conversion to biological availability was so slow, the

amount of the total phosphorus ultimately available was not as important as the rate at which it became available. The rate of usage of total phosphorus by indigenous microbial populations was measured and is reported herein.

#### LITERATURE REVIEW

A short survey of two aspects of the literature which are pertinent to the availability problem will be given here. The first section of the literature to be surveyed is concerned with the transport of total phosphorus in a river system. Cahill et al (1974) studied the phosphorus dynamics in the Brandywine River and found that the orthophosphorus concentration decreased with increasing flow and that the total phosphorus increased with flow. Enviro Control (1972) found that for most rivers this same phenomena was observed. They called the decreased orthophosphorus concentration with increasing flow the "dilution effect" and the increasing total phosphorus concentration with increasing flow was labeled the "runoff effect". Enviro Control proposes that the increase in total phosphorus concentration results from the influx of phosphorus laden waters into the river system. In contrast, Keup (1968) contends that this total phosphorus measured at a given point in a stream primarily originated from the streambottom, bank, and flood plain of the upstream river. Verhoff and Melfi (1977) have demonstrated that the most likely explanation for the known relationship of total phosphorus to flow is the theory wherein the total phosphorus passing a downstream point in

the stream came from the streambed, bank, or flood plains where it was deposited by a previous storm. Thus, the total phosphorus material is primarily associated with the fine inorganic and organic particles located in the riverbed.

As was stated previously, there has been little work done on the availability of total phosphorus from storm water. However, since it was thought that this total phosphorus originated from the river sediments, and since lake sediments might be similar to river sediments, a literature review for availability from lake sediments could be beneficial. The usual technique for the measurement of availability involves the removal of sediment from the lake and the placing of the lake sediment along with a particular algal species in a vessel and then watching the growth of the algae. Fitzgerald, (1970) separated the algal species from the Wisconsin Lake sediments with a dialysis membrane and found little growth of the algae. Golterman (1976) demonstrated that the inclusion of the dialysis bag generally limited the growth of the algae and he performed his experiments by permitting the contact of the algae and the sediments. He found that the amount of phosphorus removed by Scenedesmus was approximately equal to that which could be extracted with 0.1 M NTA. He generally incubated for about two weeks to one month and found that about five percent of what might be labeled total phosphorus was removed. Sagher et. al. (1975) investigated the availability of phosphorus from sediments of Lake Little John. They found that after two weeks the

algae had stopped growing and they measured the percent of total phosphorus incorporated into the algae after one, two, and three weeks. The maximum removal appeared to be in the range of 70 percent.

From the literature, it appeared that the material transported from storms came from river and flood plain sediments and that the available phosphorus might be released in about one month. The experiments were designed based upon this information. As was stated previously, the experiments proved that the total phosphorus was not similar to that found in lake sediments and that the fraction of total phosphorus biologically available was not as important as the rate of utilization of total phosphorus by microbial populations.

#### METHODS AND MATERIALS

The first step in this experiment required proper preparation of the laboratory. Five gallon pickle jars with their necks removed were found to provide adequate culture vessels and fluorescent workbench lamps suspended at a height from which they provided 400-foot candles at the liquid's surface were used as the light source. Stock cultures of Selenastrum capricarnutum and Microcystis aeruginosa were secured from the Corvallis EPA Lab and cultured in stock solutions before being phosphorus starved for 5-10 days in preparation for inoculation into the test sample.



Since test samples were late in arriving, local waters were collected for preliminary tests, but these waters stimulated virtually no growth so were of almost no value. It was decided to start early Honey Creek samples as soon as they arrived in an attempt to make some preliminary observations. From these it was observed that although aeration tended to make the vessel appear more active, a floc similar to activated sludge was formed making separation of biological and fixed solids impractical. To encourage suspended growth it was thought that darkening the vessel's sides might limit the light reaching the settled solids in the vessel and discourage growth in the solids. Although this did not increase the suspended biological solids present, it did seem to encourage more growth on the sides of the culture vessel which could be scraped off and analyzed. For this reason, it was decided to darken the sides of Tank 2 and Tank 3 of each sample from the bottom to approximately one-half their liquid's depth. It was also thought that a plate suspended in the sample might further darken the bottom and this was attempted with the Cattaraugus Tank 2 and Tank 3 samples, but when no desirable effects were noticed after 15 weeks, the plates were removed and not used in any other tests.

Further, the emphasis of the study was directed toward measuring the rate of total phosphorus conversion to available phosphorus. This rate can of course be dependent upon the concentration of other substances in the river water. It was decided not to add other

macro or micro nutrients; thus the measured rate would be somewhat indicative of that which might be expected in nature. Measurements of nitrogen and carbon suggested that these macronutrients would not be limiting. Several of the micronutrients were also known not to be limiting. It is not suspected that toxic materials would be present in the river storm water to prohibit growth. Thus, the major limitation to phosphorus conversion appeared to be the physical state of the phosphorus itself.

The variables analyzed and methods used are summarized in Table 1. The first two of these variables, DO and pH were checked frequently by immersing the respective electrode into the growth vessel then gently swirling the electrode and reading the meter value. The other tests were performed on aliquots drawn from the original sample.

The following laboratory procedures were followed with the test samples:

- a. Twelve to fourteen liters of sample were poured into a test vessel. This vessel was then incubated at room temperature (20°C-25°C) in 24-hour light conditions. A light intensity of approximately 400-foot candles at the samples surface was provided by fluorescent bulbs. The samples were covered with Glad Wrap to inhibit both evaporation and the entry of insects into the samples.

- b. Aliquots of the original sample were taken to establish initial conditions. All the variables in Table 1 were determined.

Table 1 - Methods of Analysis

Determination of	:	Test
DO	:	YSI Model 51 Oxygen Meter
pH	:	Beckman Model 3500 Digital pH Meter
Phosphorus	:	Persulfate Digestion Method (Std. Mthds. 425 C, III)
	:	Stannous Chloride Method (Std. Mthds. 425 E)
Solids	:	Total Residue Dried @ 103-109°C (Std. Mthds. 208 A)
	:	Total Volatile & Fixed Residue @ 550° C (Std. Mthds. 208E)
Nitrite	:	Nitrogen (Nitrite) (Std. Mthds. 420)
Nitrate	:	Nitrate Electrode Method (Std. Mthds. 419 B)

Reference: Standard Methods (1975)

c. DO and pH were frequently checked using the technique mentioned previously.

d. Harvests were made when visual observations suggested they were necessary. A centrifuge capable of handling one and one-half liters of sample at one time at speeds up to 12,000 RPM was first used. This was a rather tedious process, so when a continuous centrifuge became available it was used. Some operational difficulties were encountered with the continuous centrifuge and a snapped tube resulted in a five liter loss from the Sandusky Tank 2 sample during the 13 September 1977 extraction. It was found that a speed of 10,000 RPM was suitable once the continuous centrifuge was in working order. In the Honey Creek and Broken Sword samples, growth on the sides of the test vessel and a crusty layer on the surface of the settled solids became noticeable and was collected using acid washed razor blades and rubber gloves once the vessel was drained. Using the above techniques, the harvest schedule shown on Table 2 was followed. Harvests were analyzed for solids and phosphorus.

e. As our time ran out an effort was made to aerate our samples after  $\text{NaNO}_3$  addition to maximize growth. Aeration was for three weeks in Sandusky Tank 1 and for one week in the other test vessels.

f. Aliquots from each sample were taken and analyzed to find the solids and phosphorus still in them.

Table 2 - Harvest Schedule

Date	Day #	Day # HC & BS	Sandusky			Honey Creek			Broken Sword		
			Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3***
8/23	36	-	6 @ 10,000 RPM*								
8/29	42	-	6 @ 10,000 RPM*								
**											
9/13	57	-	6 @ 18,000 RPM								
10/16	80	23	9 @ 10,000 RPM			9 @ 10,000 RPM					
10/17	-	34				12 @ 10,000: RPM	Scrape Sides and Bottom		12 @ 10,000: RPM	Scrape Sides and Bottom	
						Scrape Sides			Scrape Side		
11/9	-	56				12 @ 10,000: RPM	Scrape Bottom		Scrape Bottom		
11/24	129	72	Scrape Sides			12 @ 10,000: RPM					
12/6	143	84				12 @ 10,000: RPM			12 @ 10,000: RPM		
12/20	-	98						Scrape Sides			

\* Centrifuge run for 10-15 minutes

\*\* All centrifuge work done after this point was done with the continuous centrifuge

\*\*\* Growth in the Cattaraugus samples was insufficient to harvest

The major handicap encountered in this experiment was the small number of samples provided for study. In an attempt to gain usable data the samples were treated with a high degree of uniformity, the darkening of the sides being the only real difference. It had been planned to refine a technique using the first series of samples by trying a variety of ideas, then using the most suitable idea in acquiring usable data with the next three series of samples, but this plan of attack was unsuitable with the samples provided.

## RESULTS AND DISCUSSION

### DO and pH Measurements

The DO and pH were monitored continuously throughout this experiment. For each sample, values were found in each vessel and these three values were averaged together to yield the data points shown on Figures 1-4.

The DO curves in these figures exhibit lag time before maximum DO is reached. If DO levels are an indicator of photosynthetic activity one would then assume that there is a lag time of approximately 15 to 35 days before a steady state microbial activity is reached. Another point brought out by the DO in the Cattaraugus curve (Figure 1) is the lack of microbial activity in the vessel. This unchanging dissolved oxygen (DO) agrees with the absence of algal activity noted in the sample over the duration of the experiment.

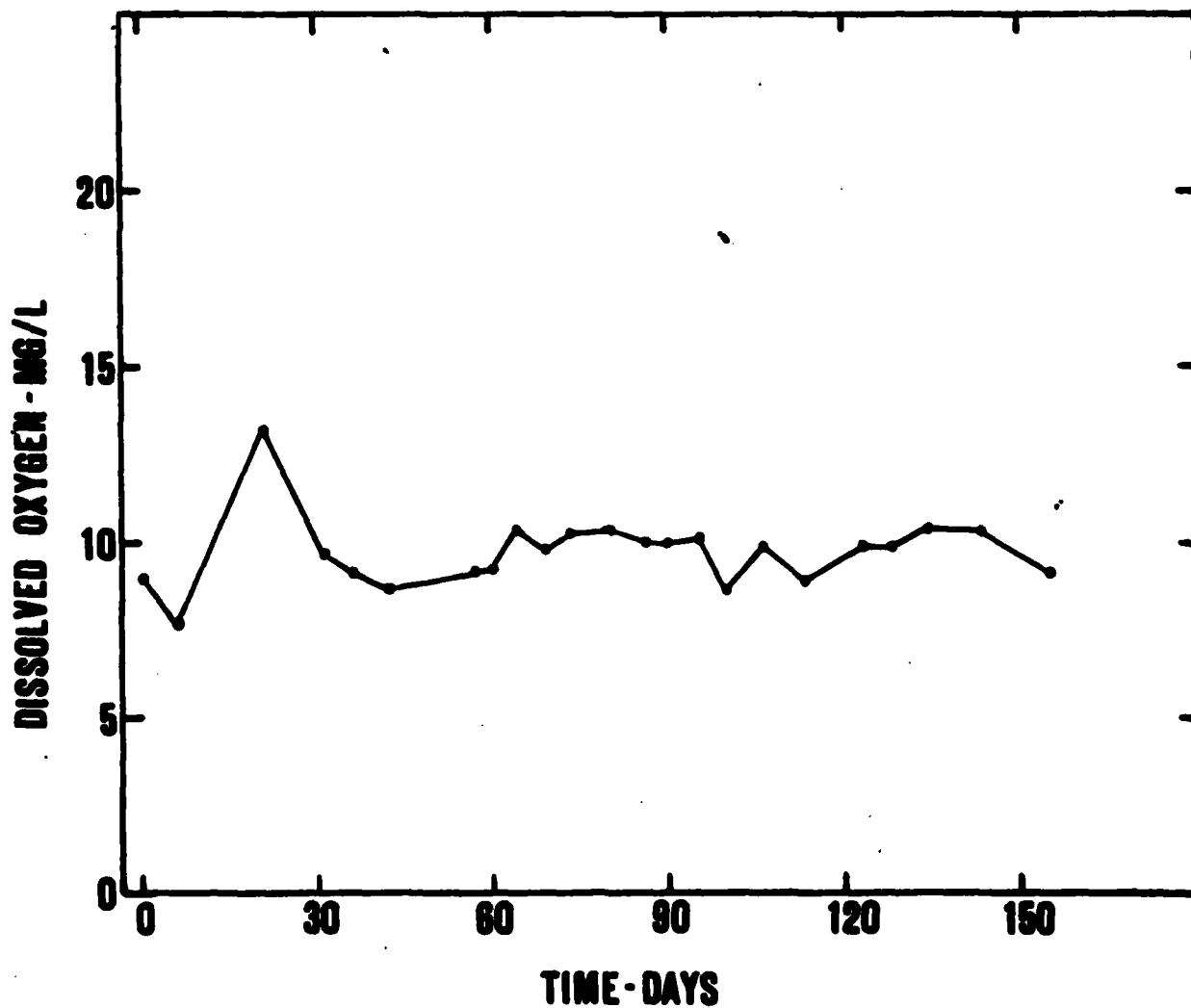
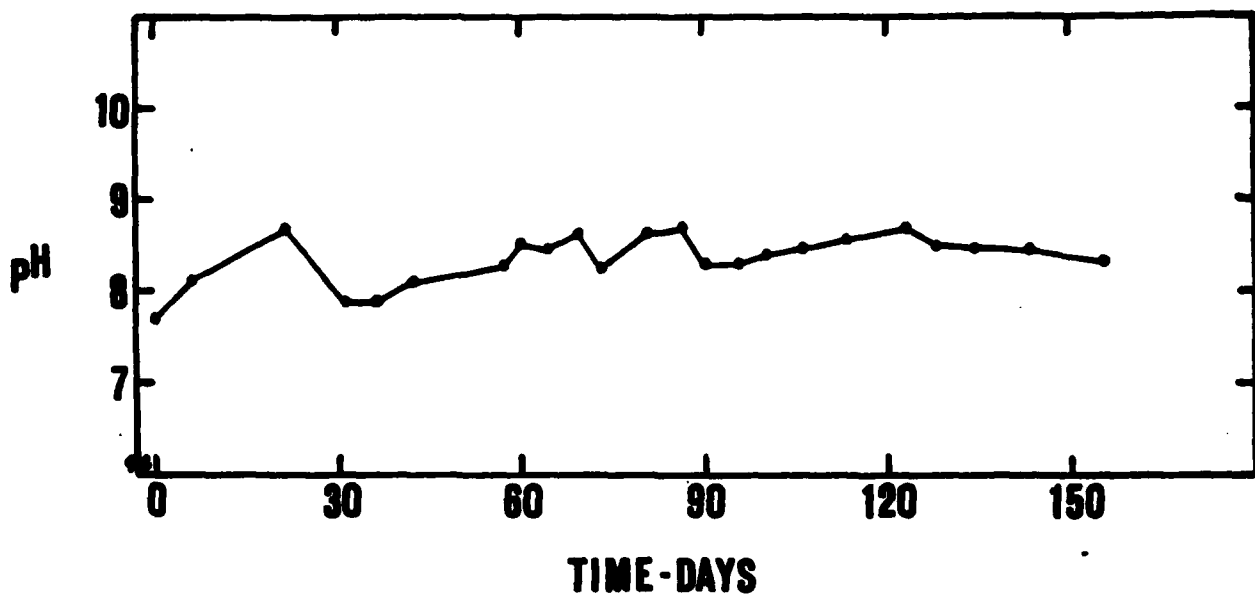


Figure 1. Dissolved Oxygen and pH vs. Time (Cattaraugus River Samples).

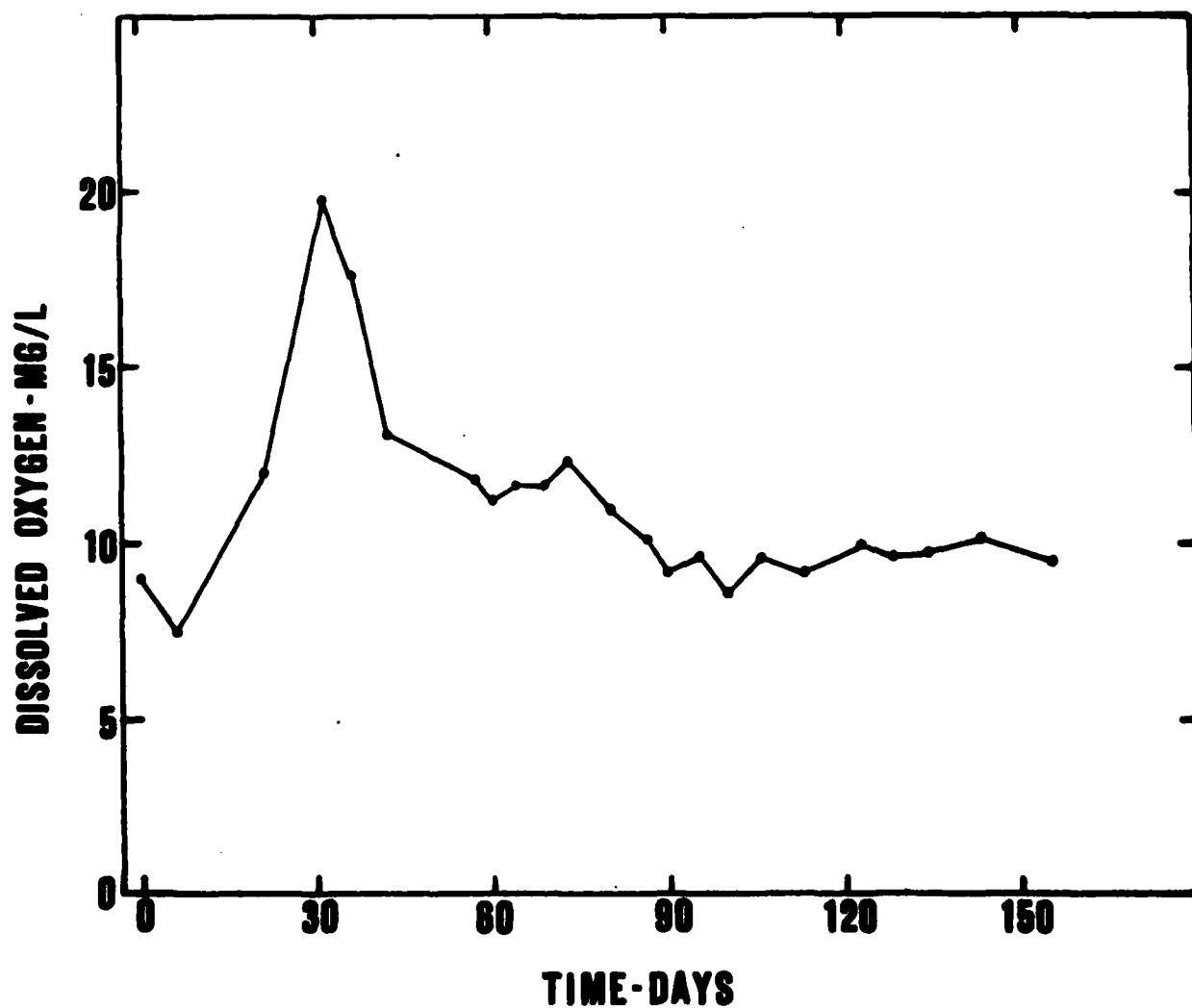
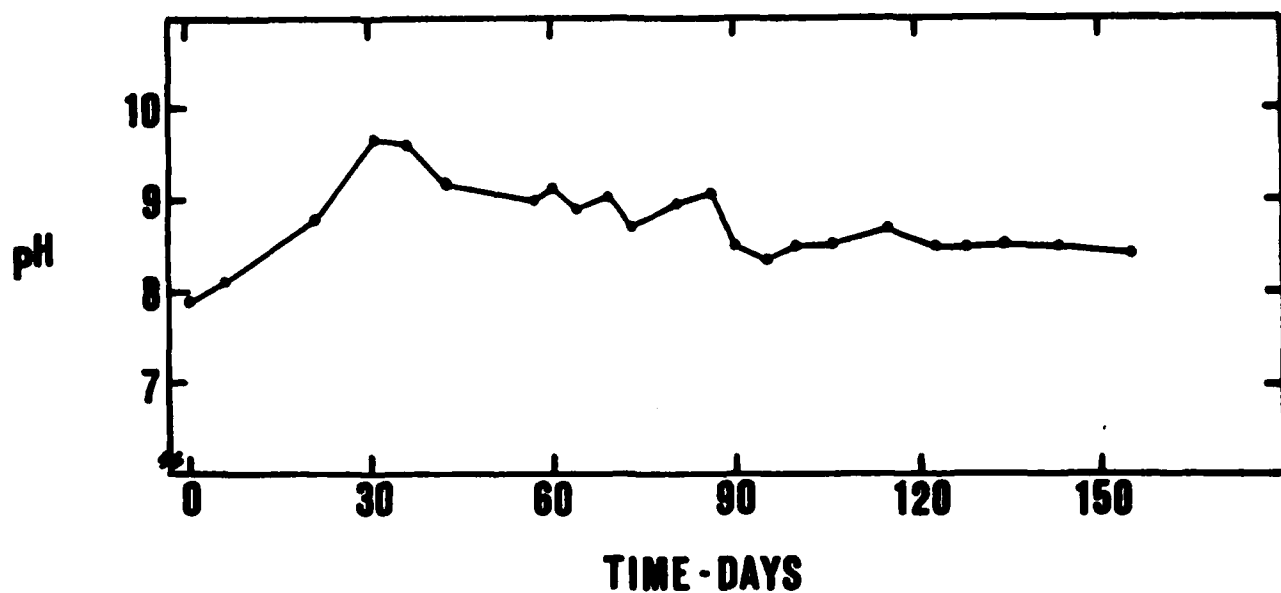


Figure 2. Dissolved Oxygen and pH vs. Time (Sandusky River Samples).



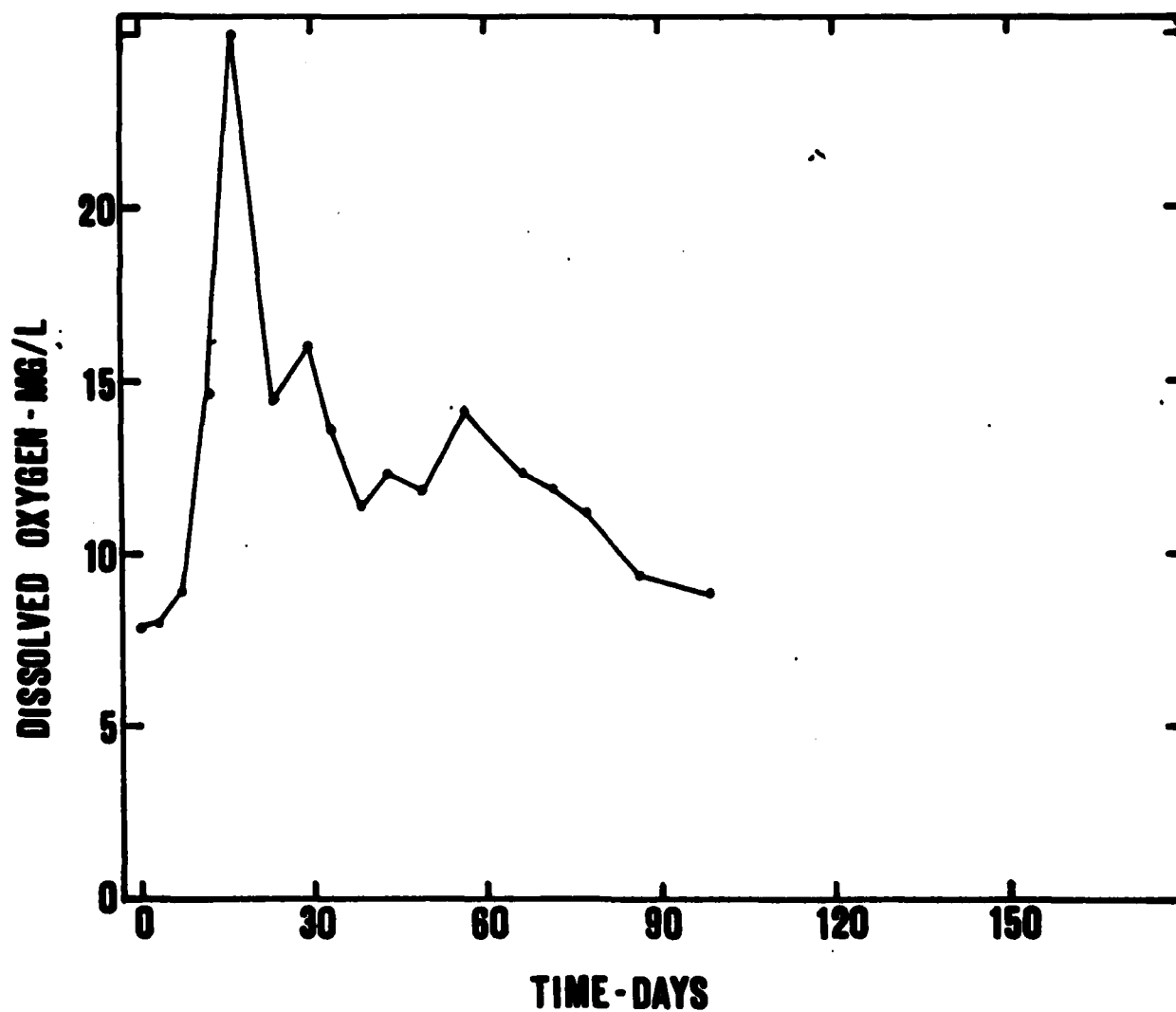
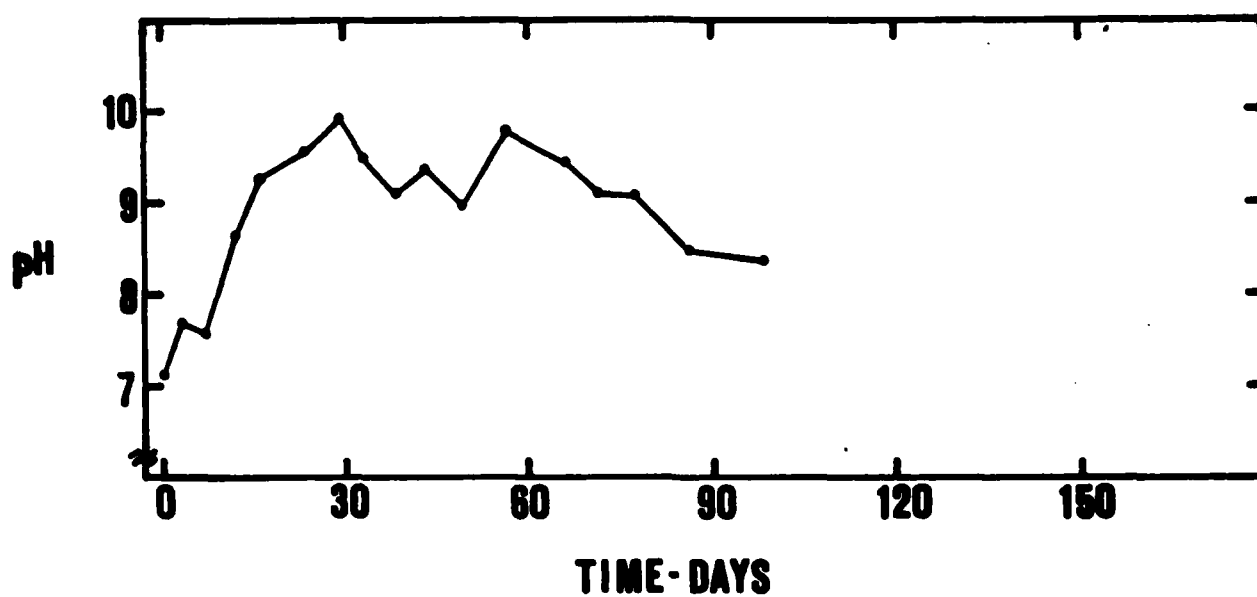


Figure 3. Dissolved Oxygen and pH vs. Time  
(Honey Creek Samples).

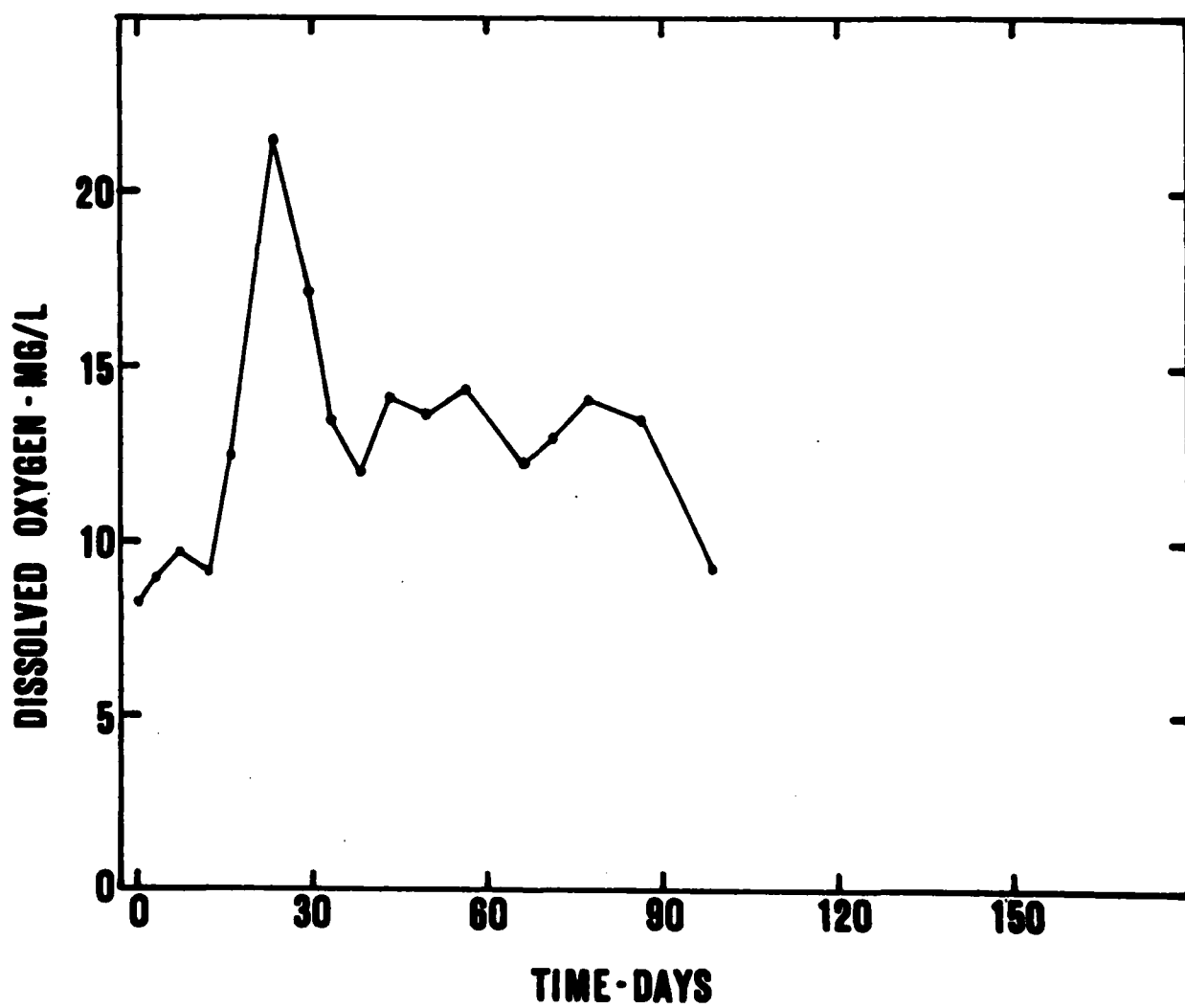
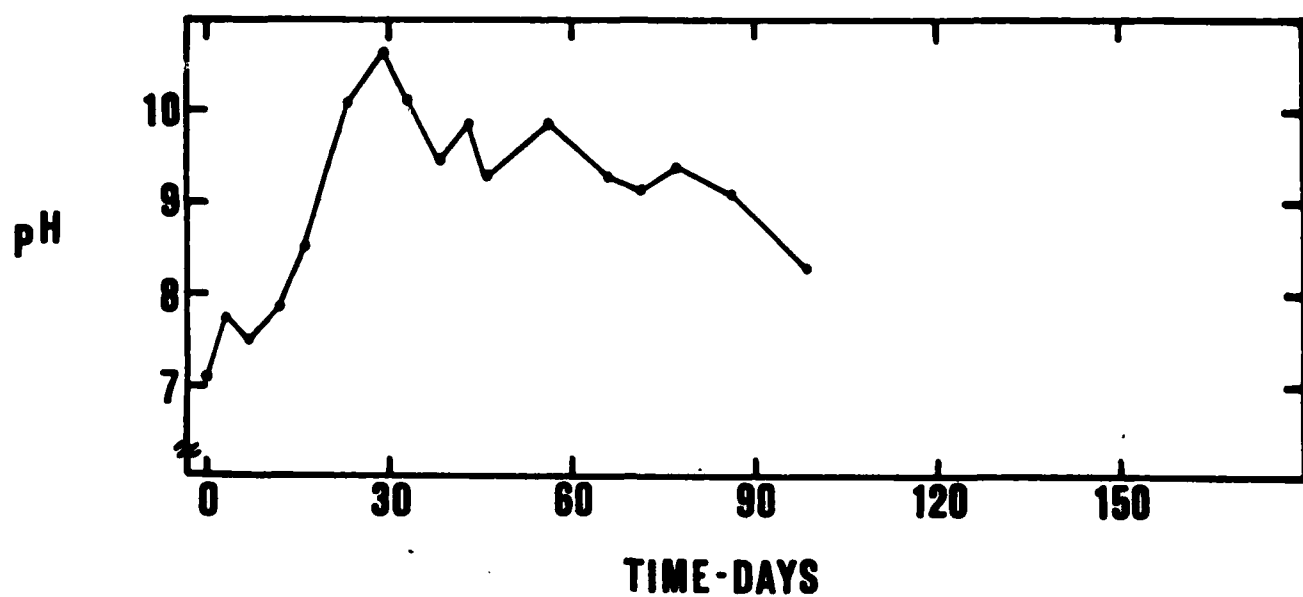


Figure 4. Dissolved Oxygen and pH vs. Time  
(Broken Sword River Samples).

The pH data shows that the samples rose above the 8.5 maximum recommended in the Algal Assay Procedure Bottle Test (1971). We elected not to artificially lower the pH when it exceeded this value; letting the system be more self-regulating by allowing it to respond naturally to the situation. As the figures indicate the pH did finally return to the 8.5 range.

#### Biological Removal of Phosphorus by Algal Harvests

The parameters measured on the river water initially placed in the vessel are compiled in Table 3 (except for the DO and pH data which is shown at T = 0 on Figures 1-4). This base data provides the starting points in Table 4 which presents the extraction data. At time equals zero in Table 4, the total suspended solids (mg/l and phosphorus (mg/l) from Table 3 were multiplied by the test samples volume to give the suspended solids and phosphorus in milligrams originally in the test vessel. As an extraction was made according to the schedule shown in Table 2, the following calculations were made and the results entered in the appropriate column of Table 4.

$$\frac{\text{Wt. Volatile Solids Removed}}{.75} = \text{Wt. Algae Removed}$$

The average percentage of algal cells which were volatile solids was determined to be 76.6 from experiments using mixed algal culture. Four different samples of this culture were assayed for volatile and fixed solids. The range of volatile solids found for these four

Table 3 - Initial Data

Fraction	Sandusky			Cattaraugus			Honey Creek			Broken Sword		
	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3
<b>Solids (mg/l)</b>												
Total	782	796	758	5,768	4,698	5,844	1,818	1,636	2,030	1,502	1,492	1,468
Fixed	620	620	592	5,396	4,352	5,454	1,492	1,346	1,694	1,262	1,270	1,230
Volatile	162	176	166	372	346	390	326	290	336	240	222	238
Suspended	442	454	436	5,560	4,498	5,636	1,468	1,268	1,683	1,188	1,186	1,184
Fixed	406	404	398	5,254	4,218	5,316	1,316	1,154	1,546	1,094	1,114	1,088
Volatile	36	50	38	306	280	320	152	114	142	94	72	96
Dissolved	340	342	322	208	200	208	350	368	342	314	306	284
Volatile	126	126	128	66	66	70	174	176	194	146	150	142
<b>Phosphorus (mg/l)</b>												
Total	.65	.63	.63	2.29	2.23	2.71	1.06	1.02	1.15	.95	.97	.94
Ortho	.15	.15	.15	.05	.05	.05	.10	.10	.08	.07	.07	.07
<b>Nitrogen</b>												
NO <sub>3</sub> (mg NO <sub>3</sub> -N/l)	6.1	5.9	5.7	1.2	1.3	0.9	9.7	9.4	8.6	13	13	13
NO <sub>2</sub> (mg NO <sub>2</sub> -N/l)	16	17.6	21.4	14.1	16.0	17.6	3.5	2	2.8	2.2	2	2.0

Table 4 - Extraction Data

Date	Loc. & Mts.	Fraction	Sandy			Honey Creek			Broken Board					
			Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3			
7/13	0/-	Suspended Solids (SS)	6,108	100	6,356	100	6,104	100						
		Phosphorus (P)	9.1	100	8.8	100	8.8	100						
8/23	136/-	Monial SS	0	0	0	0	0	0						
		Algae	89	-	129	-	94	-						
		P	.24	2.6	.26	3.0	.24	2.7						
8/29	42/-	Monial SS	0	0	10	0.2	0	0						
		Algae	65	-	55	-	70	-						
		P	.17	1.9	.11	1.2	.17	1.9						
9/13	157/0	Monial SS	0	0	14	0.2	30	0.5	20,552	100	17,752	100	14,256	100
		Algae	54	-	41	-	35	-				16,604	100	17,050
		P	.10	1.1	.11	1.2	.09	1.0	14.8	100	14.3	100	13.6	100
10/6	80/23	Monial SS	0	0	63	1.0	238	3.9	49	0.2	96	0.5	73	0.3
		Algae	78	-	51	-	117	-	127	-	103	-	157	-
		P	.11	1.2	.14	1.6	.38	4.3	.39	2.6	.39	2.7	.69	4.3
10/7	191/34	Monial SS							458	2.2	371	2.1	491	2.1
		Algae							444	-	591	-	231	.69
		P							.59	4.0	.69	4.5	1.64	10.2
									.35	10.2	3.1	10.2	3.1	3.9
									26	0.2	83	0.3	83	0.5
									116	11.6	191	11.6	191	-
									5.1	5.1	5.1	5.1	5.1	3.9

Table 6. Extraction Data (Cont'd)

These points not used in calculating the "a" value mentioned later in the text.

samples is 73.3 to 78.0 percent. For convenience, the 75 percent value was used in the calculations.

This calculation assumes that all the volatile solids are algal. Another possible assumption would be that the nonalgal suspended solids have a volatile fraction equal to the initial fraction. Either of these assumptions yields approximately the same phosphorus conversion rate; hence, the simpler calculation was selected.

After the weight of algae removed was calculated, the weight of the nonalgal suspended solids removed could then be found:

$$\begin{aligned} \text{Wt. Nonalgal Suspended Solids Removed} &= \text{Wt. Suspended Solids Removed} - \text{Wt. Algae Removed} \\ \text{Percent Nonalgal Suspended Solids Removed} &= \frac{\text{Wt. Nonalgal Suspended Solids Removed}}{\text{Wt. Suspended Solids at } T = 0} \times 100 \\ \text{Percent Phosphorus Removed} &= \frac{\text{Wt. Phosphorus Removed}}{\text{Wt. Phosphorus at } T = 0} \end{aligned}$$

To analyze the data in Table 4, a series of plots were constructed in which the cumulative percent phosphorus removed was compared with time. Figure 5 shows this plot for the Honey Creek sample. A least squares analysis of the form  $y = ax$  in which  $a$ , the slope, is equal to the removal rate was made for each sample. A 90 percent confidence interval of the form:

$$B = b \pm t \frac{E(Y_i - ax_i)^2}{(n-2)E(x_i - \bar{x})^2}$$

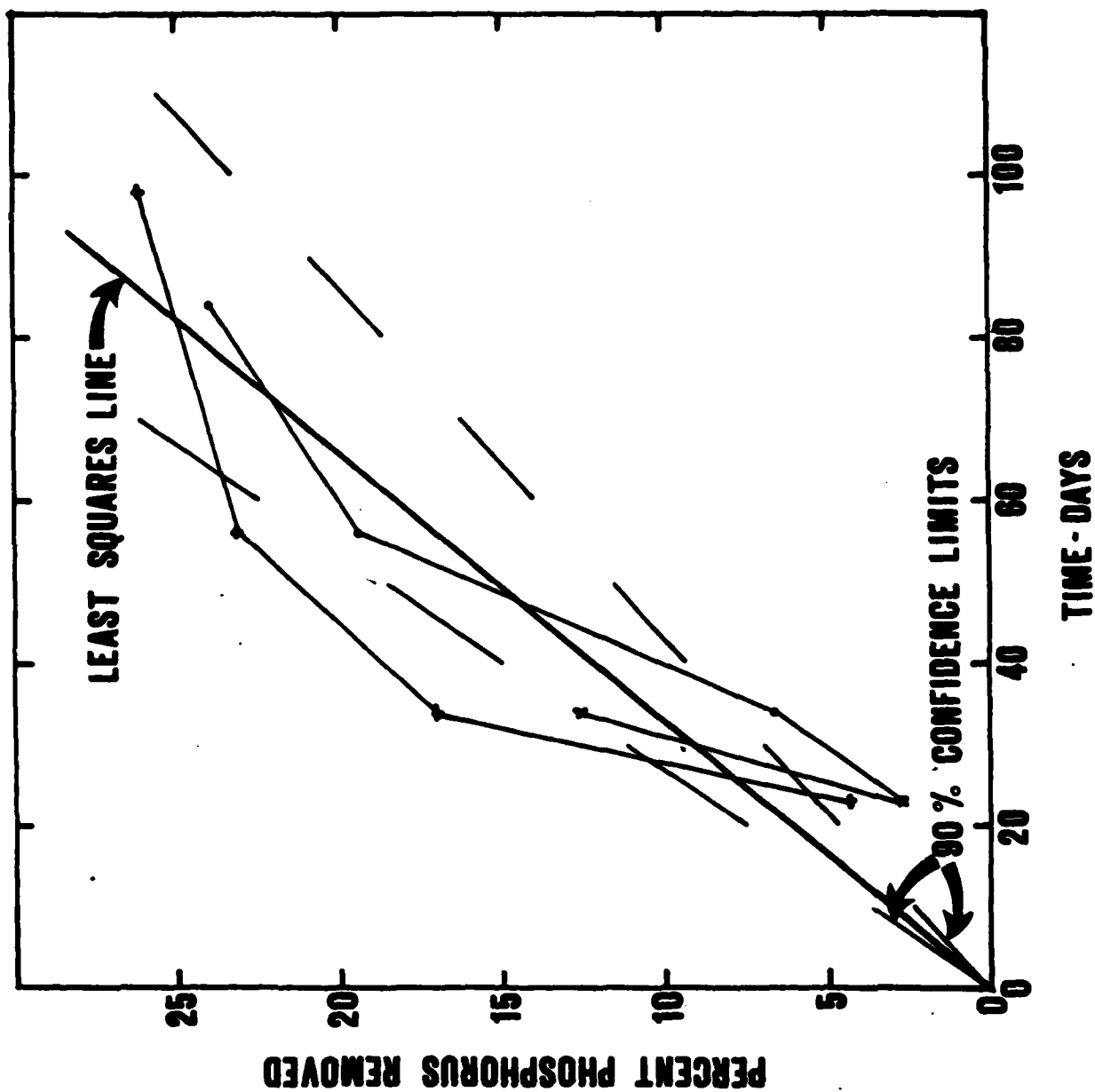


Figure 5. Percent Phosphorus Removal vs. Time (Honey Creek Samples;  $\circ$  = Tank 1;  $\times$  = Tank 2;  $+$  = Tank 3).



was calculated and appears on Figure 5 in the form of broken lines. The uptake rates found using this method of analysis are presented in Table 5.

Table 5 - Removal Rates for Extraction Data with No Consideration of Nonalgal Solids Removal

	: Sandusky	: Honey Creek	: Broken Sword
"a" value	: .087	: .301	: .276
% P removed/day	:	:	:

This method of analysis presumed that all the total phosphorus was associated with the microbe when in fact some of it was removed in the nonalgal suspended solids portion of the extractions. To account for phosphorus in these nonalgal suspended solids, the assumption that the sediment associated phosphorus<sup>1</sup> originally in the sample was evenly distributed among the suspended solids in the sample was made. This meant that the percent nonalgal suspended solids removed also represented the percent sediment associated phosphorus removed in the nonalgal suspended solids and allowed the following calculation to be made:

$$\begin{aligned} \text{Percent Phosphorus} &= \text{Percent Phosphorus} - \left[ \text{Percent Nonalgal} \right. \\ \text{Removed by Algae} &\quad \text{Removed} \quad \left. \text{Suspended Solids Removed} \right. \\ &\quad \times \left. \frac{\text{Wt. Sediment Associated Phosphorus at T = 0}}{\text{Wt. Total Phosphorus at T = 0}} \right] \end{aligned}$$

<sup>1</sup> Sediment associated phosphorus equals initial total phosphorus concentration minus the initial ortho phosphorus concentration.

A series of plots comparing the cumulative percent phosphorus removed by the algae and time was then made for each sample (Figures 6-8). The same least squares and 90 percent confidence interval as was used previously were then calculated and drawn on Figures 6-8. This method of calculation seemed more reasonable so a further calculation to find an uptake rate in terms of  $\frac{\text{mg Phosphorus Removed by Algae}}{\text{gm Fixed Solid} \times \text{Day}}$

was made using the formula:

$$\text{Uptake Rate } \frac{\text{mg P Removed by Algae}}{\text{gm Fixed Solids} \times \text{Day}} = \left[ \frac{\text{Percent P Removed by Algae}}{\text{Day}} \right] \times \left[ \frac{\text{mg P Originally}}{\text{gm FS Originally}} \right]$$

The percent removal rates and uptake rates are both summarized by Table 6.

Table 6 - Removal Rates for Extraction Data  
Considering Nonalgal Solids Removal

	: Sandusky	: Honey Creek	: Broken Sword
Removal Rate	:	:	:
<u>% P removed by Algae</u>	: .087	: .268	: .217
day	:	:	:
95% Confidence Interval	: .072 - .102	: .194 - .324	: .041 - .392
Update Rate	:	:	:
<u>mg P removed by Algae</u>	: .092	: .191	: .164
gm solids	:	:	:
90% Confidence Interval	: .076 - .108	: .138 - .244	: .031 - .296
	:	:	:

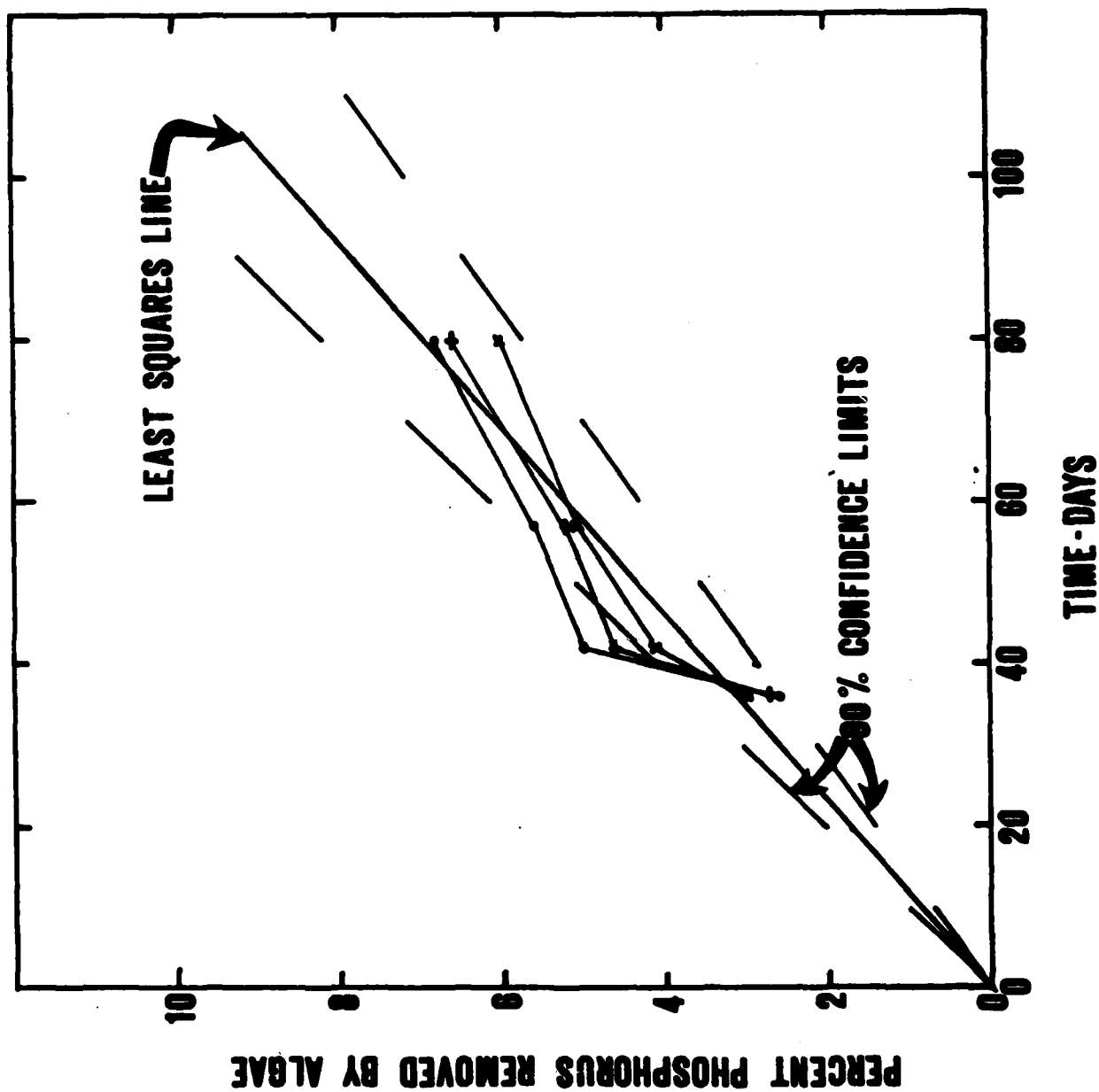


Figure 6. Percent Phosphorus Removal by Algae vs. Time (Sandusky River Samples; • = Tank 1; X = Tank 2; + = Tank 3).

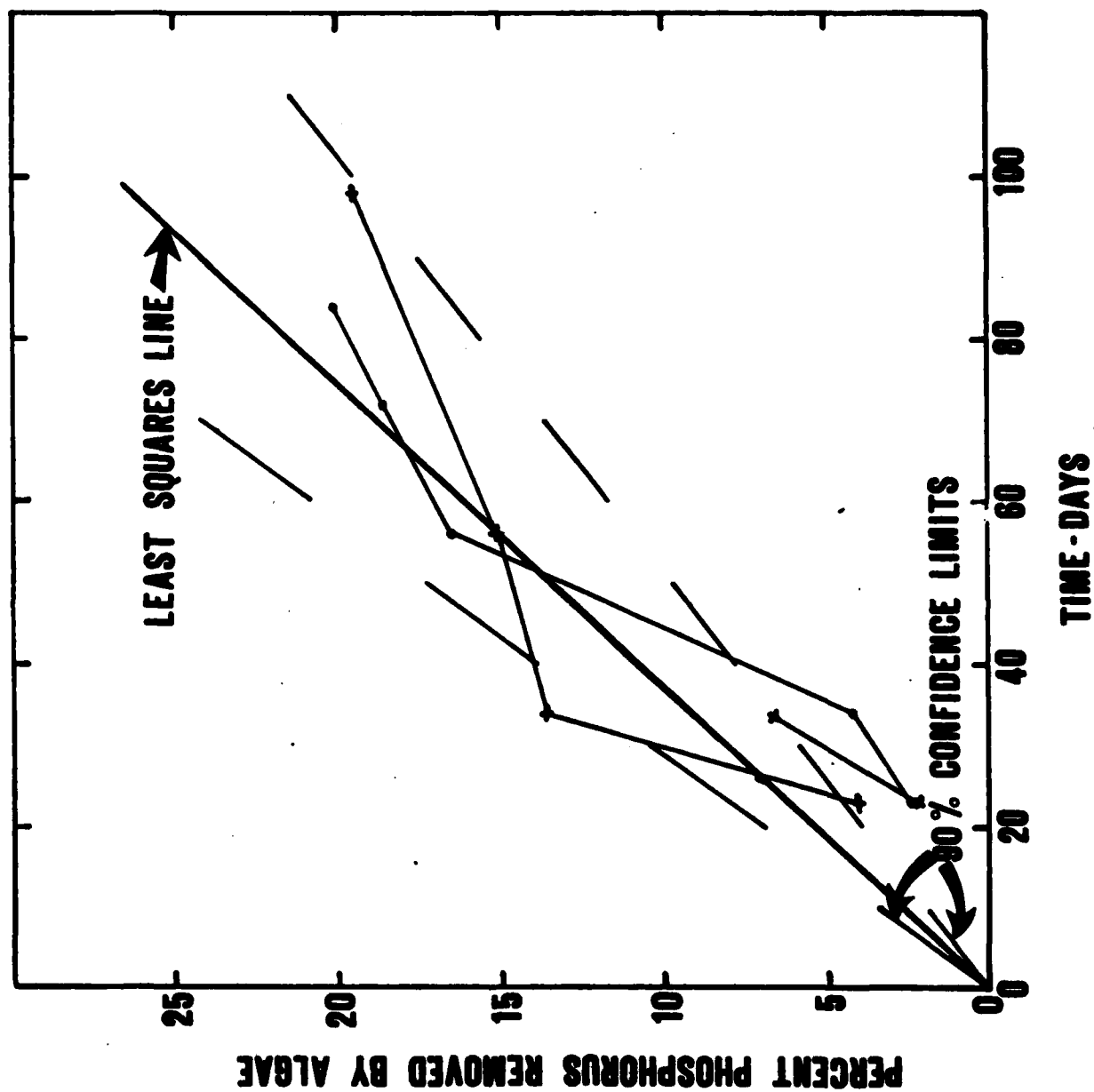


Figure 7. Percent Phosphorus Removal by Algae vs. Time (Honey Creek Samples; ° = Tank 1 X = Tank 2; + = Tank 3).

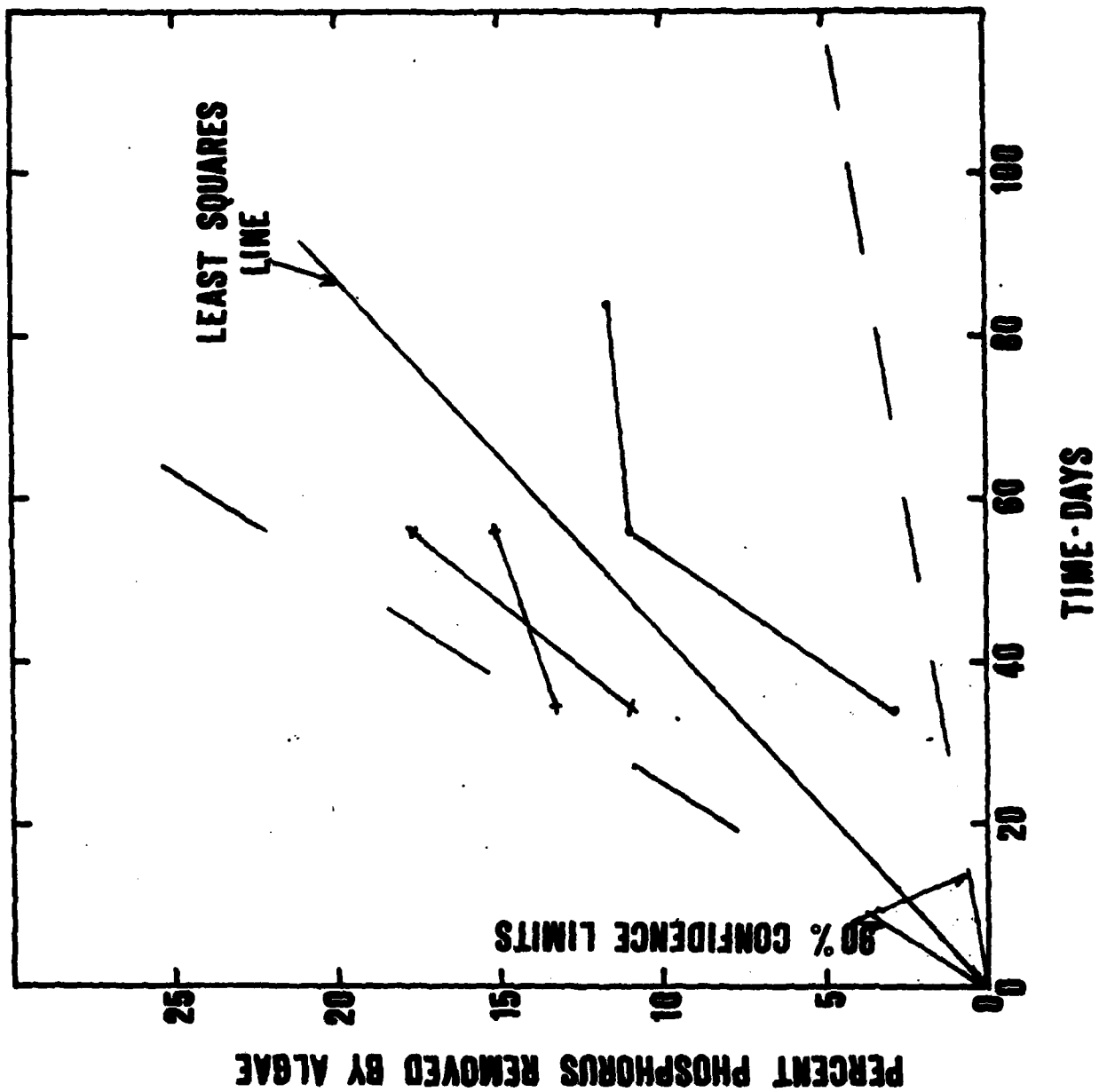


Figure 8. Percent Phosphorus Removal by Algae  
vs. Time (Broken Sword River Samples;  
• = Tank 1; X = Tank 2; + = Tank 3).

### Check of Lag Phase

A check of the Honey Creek "a" value using the least squares formula of  $y = ax + b$  was then made to check the  $y = ax$  fit for accuracy. This type of formula would provide better fit if the lag were significant. The "a" value of .226 and "b" value of -.13 for the  $y = ax + b$  test as compared to the "a" value of .268 and "b" value of 0 for the  $y = ax$  test seems to indicate that the assumption of  $b = 0$  was valid.

### Final Measurements of Materials

Final measurements were made after adjusting the sample volume to its original level if necessary. The sample was thoroughly mixed and aliquots were removed and tested for solids and phosphorus (Table 7). These results were compared to the original data to find the percentages lost during the experiment based upon the final and initial concentration. These percentages along with those associated with extractions are listed in Table 8.

As can be seen, there are some significant differences between the percent total phosphorus and suspended solids removed as calculated by the two methods. The difference in the percent phosphorus removed and percent fixed solids removed can be explained by:

a. Small errors in analysis. The percent difference in the total P removed minus the total extracted may appear large, but this

Table 7 - Final Date 12/21, Day 156/99

Fraction	Sandusky			Cattaraugus			Honey Creek			Broken Sword		
	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3
Solids mg/l												
Total	-	620	754	3,628	3,566	4,440	1,822	1,410	1,692	1,416	1,450	1,314
Fixed	-	450	550	3,330	3,426	4,090	1,558	1,170	1,448	1,144	1,190	1,062
Volatile	-	170	204	298	320	350	264	240	244	272	260	252
X Fixed Lost:		27.4	7.1	38.3	21.3	25.0	-	13.1	14.5	9.3	6.3	13.7
Phosphorus (mg/l)												
Total	-	.24	.425	1.35	1.1	1.9	.52	.67	.78	.65	.555	.58
X P Lost	-	60.3	32.5	41.0	50.7	29.9	50.9	34.3	32.2	31.6	42.7	38.3

Table 8 - Differences in Extraction Data and Final Data

	Sandusky			Honey Creek			Broken Sword											
	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3	Tank 1	Tank 2	Tank 3									
	P	FS	P	FS	P	FS	P	FS	P	FS	P	FS	P	FS	P	FS		
1. Z Removed with extractions	7.7	0.6	7.0	1.0	12.7	5.0	24.0	3.9	12.6	5.9	26.2	9.5	18.4	6.7	24.9	7.2	21.9	6.8
2. Z Removed total:	60.3	7.4	32.5	7.1	50.9	0	34.3	13.1	32.2	14.5	31.6	9.3	42.7	6.3	38.3	13.7		
2-1	*		19.8	2.1	26.9	3.9	21.7	7.2	6.0	5.0	13.2	1.6	17.8	0.9	16.4	6.9		
This considered invalid due to spillage during testing																		

\* This considered invalid due to spillage during testing



error when multiplied by the original phosphate concentrations yields a total error of .97 mg/l. When this error is distributed over the 27 extractions made, an error of 0.04 mg/l per sample is realized. Most samples had to be diluted 1:10 for analysis, so an average analytical error of .004 mg/l could lead to the differences noted. However, it is unlikely that all errors are systematically biased.

b. A loss of the side of vessel above the waterline and on the covers during the last aeration. This is probably the main cause of the errors since the smaller particles containing the larger portion of the total phosphorus would be lost. Hence, the total phosphorus should yield a larger percentage removed than the fixed solids as is found from experiment.

The uptake rate values which probably best fit the experiment are listed in Table 6 extraction experiments. Thus, a realistic value for the uptake rate would be 0.2 percent per day. Even if the final values are considered, the best estimate of the uptake rate would be approximately 0.4 percent per day. Both of these rates are much lower than was expected and lower than those used in models found in the literature.

### Conclusions

The absence of harvestable growth and the lower DO and pH values for the Cattaraugus samples indicate that the Cattaraugus River water was far less suitable for biological activity than the Sandusky, Honey

Creek, and Broken Sword waters. Presumably, the total phosphorus in the Cattaraugus is less available than that of the other creeks.

Phosphorus removal by the algae appears to take place at a rate less than .40 percent P/day. This is significantly less than the value of five to 10 percent P/day often given for lake sediments. This slow rate implies that biological activity is capable of utilizing total phosphorus from river storm flows for a year or two after it has flushed into the lake. This long time period indicates that the rate of release of total phosphorus is more important than the ultimate total availability of the total phosphorus.

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